

CLEAN WATER ACT (CWA)
NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM (NPDES)
SPILL PREVENTION CONTROL AND COUNTERMEASURES (SPCC)

MULTI-MEDIA COMPLIANCE INVESTIGATION

ASHLAND PETROLEUM REFINERY
Catlettsburg, Kentucky

Facility Address

Ashland Petroleum Company
8023 Crider Drive
Catlettsburg, Kentucky 41129

Investigation Dates

October 28 through November 8, 1996

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MEDIA REPORT

INTRODUCTION

At the request of EPA Region 4, NEIC conducted a multimedia compliance investigation of the Ashland petroleum refinery located in Catlettsburg, Kentucky. This report discusses Clean Water Act (CWA) issues and compliance with the applicable regulatory requirements at Ashland including National Pollutant Discharge Elimination System (NPDES) and Spill Prevention, Control, and Countermeasures (SPCC) programs.

REGULATORY SUMMARY

The Ashland refinery is regulated by a National Pollutant Discharge Elimination System (NPDES) permit because they discharge treated wastewater and stormwater to the Big Sandy River. Ashland also discharges stormwater to Chadwick Creek. Ashland operates a petroleum refinery (Standard Industrial Code 2911) and is, therefore, subject to the following Clean Water Act regulation: Effluent Guidelines and Standards for the Petroleum Refining Point Source Category [40 CFR Part 419].

EPA Region 4 has delegated the NPDES program to the Kentucky Department of Environmental Protection (KYDEP). On June 11, 1996, KYDEP issued NPDES permit number KY0000388 [Appendix A], establishing effluent limitations for the Ashland refinery. This permit was effective on August 1, 1996, and has an expiration date of July 31, 2001. The permit was based on the above referenced Effluent Guidelines, water quality standards, and best professional judgement (BPJ).

NPDES permit KY0000388 authorizes the discharge of wastewater from the Ashland refinery at 25 outfalls. A description of the outfalls, which was included in Ashland's May 1994 permit application, is contained in Appendix B.

Refinery process wastewater is discharged from Outfall 001 to the Big Sandy River. This discharge also contains process wastewater from Ashland Chemical, treated sanitary wastewater, cooling tower blowdown, contaminated stormwater runoff, rail car cleaning, hydrostatic test water, and groundwater from recovery wells.

Sanitary wastewater generated at Ashland is treated in small package treatment plants located throughout the facility. These package plants consist of an aerobic tank, clarifier, and chlorine contact chamber. Effluent from these package plants is monitored at internal outfalls (Outfall numbers 008 to 014, 016 to 019, and 024). Normally, all the package treatment plant effluent receives additional treatment at the main refinery wastewater treatment plant prior to being discharged to the Big Sandy River via Outfall 001. However, the package plant at the old H-Coal facility (Internal Outfall 016) is authorized to discharge directly to the Big Sandy River via Outfall 015.

Contaminated stormwater at the plant is directed to the main process wastewater treatment plant and discharged via Outfall 001. Noncontaminated stormwater from the plant is discharged via Outfalls 004, 005, 006, 015, 021, 022, and 023 to the Big Sandy River and via Outfalls 007 and 020 to Chadwick Creek. The permit also authorizes the periodic discharge of hydrostatic test water from some of the stormwater outfalls. In addition to stormwater, the permit also authorizes the discharge of noncontact cooling water, water

treatment filter backwash, and ion exchange regenerant backwash at Outfall 006.

Supernatant from the lime clarifier sludge ponds is authorized to be discharged via Outfall 002 to the Big Sandy River. This water can also be pumped back to the refinery's raw water settling ponds. Outfall 003 authorizes the discharge of noncontact cooling water to the Big Sandy River; however, this outfall is not normally in use. Outfall 025 authorizes the discharge of overflow water from the refinery's raw water settling pond back to the Big Sandy River.

Pounds per day permit limitations are established by KYDEP, based upon the federal effluent guidelines, for the following parameters at Outfall 001: biochemical oxygen demand (BOD), total suspended solids (TSS), chemical oxygen demand (COD), oil and grease, phenolic compounds, ammonia, and sulfide. Total chromium and hexavalent chromium limits were not established in the permit, despite the fact that effluent guidelines are established for these parameters. The rationale for this decision is that the basis for these effluent guidelines were the use of chromium additives in cooling towers and Ashland does not use any chromium compounds in the cooling towers.

Concentration based limits are established in the permit, based upon water quality standards and BPJ, for the following pollutant parameters at Outfall 001: nickel, lead, cyanide, arsenic, beryllium, zinc, temperature, and toxicity. In addition, an acceptable pH range for discharge is also established.

Permit limitations are established for the following parameters for the stormwater discharge outfalls: total organic carbon (TOC), oil and grease, and pH. Monitoring is also required for TSS and flow. [Outfall 006 also regulates

temperature and chlorides due to the additional discharge from the ion exchange backwash and cooling water.] Permit limitations are established for TSS at Outfall 002, temperature and TOC at Outfall 003, and total residual chlorine at Outfall 025.

No permit limitations are established at the internal outfalls for the sanitary package treatment plants, but monitoring is required for flow and fecal coliform. [The H-Coal package plant (Outfall 016) is regulated for TSS and BOD when discharge is directly to the Big Sandy River via Outfall 015]. The previous permit regulated fecal coliform at each of the internal outfalls. These limitations were removed in the most recent permit, because the effluent receives further biological treatment (but not chlorination) in the main process wastewater treatment plant. It should be noted that there are no permit limitations established for Outfall 001 for fecal coliform; however, it is unlikely coliform would be detected after dilution with the refinery process wastewater. It is not clear why fecal coliform limits were not established for Outfall 016 when the sanitary effluent is discharged directly to the Big Sandy River via Outfall 015.

The specific rationales for the effluent limitations are contained in a fact sheet, which is included as an attachment to the NPDES permit. The production-based limitations contained in the federal petroleum refining regulations were the basis for the pounds per day effluent limitations established in the NPDES permit. The KYDEP classified Ashland as an integrated refinery subject to 40 CFR Part 419, Subpart E.

All the stormwater discharges from the Ashland refinery are identified and regulated by NPDES permit KY0000388. Therefore, this facility does not require a separate NPDES stormwater permit.

NPDES permit KY0000388 was previously adopted on November 1, 1989, and contained an expiration date of October 31, 1994. This permit was subsequently modified, with the last modification occurring on April 27, 1993 [Appendix C]. Ashland submitted a complete application for a renewed permit on May 31, 1994. KYDEP did not issue a permit renewal until June 11, 1996 with an effective date of August 1, 1996. Therefore, the April 27, 1993 modified permit remained in effect until August 1, 1996.

Ashland has greater than 1,320 gallons of aboveground oil storage capacity and, because of their location, could reasonably be expected to discharge oil into waters of the United States. Therefore, this facility is required to develop and certify an SPCC Plan. Ashland has developed an SPCC plan, and the most recent revision was completed and certified on October 1, 1996. In accordance with 40 CFR § 112.3(d), this plan was certified by Joe Hissom, a registered professional engineer. The previous edition of the SPCC plan was certified on March 17, 1994 by Bruce Churton, a registered professional engineer.

The Oil Pollution Act of 1990 required facilities, that could reasonably be expected to discharge oil to waters of the United States, to develop a Spill Preparedness and Emergency Response Plan by February 1993. Ashland submitted their original Plan to EPA Region 4 in February 1993. Revisions to the plan were made in January 1995 and October 1996.

WATER SUPPLY AND WASTEWATER GENERATION

Ashland pumps water from the Big Sandy River for use as noncontact cooling water, industrial process needs, and boiler water. Water is pumped from the Big Sandy River to the raw water settling pond, where suspended solids are allowed to gravity settle. Chlorine is periodically added to the pond to prevent algae growth. Water from the raw water settling pond is pumped to two clarifiers, where lime and a polymer are added for softening and additional solids removal. Lime sludge from the clarifiers is pumped to two lime sludge settling ponds. The clarifier effluent is directed to holding tanks, where sulfuric acid is added for pH adjustment. From the holding tanks, water can be used directly for refinery needs and cooling tower make-up water, or pumped to the boiler water treatment facility. Boiler feed water is further treated in anthracite pressure filters, cation exchange units, and reaerated.

Potable water for refinery needs is purchased from the local municipality; therefore, Ashland is not subject to the public water system regulations adopted pursuant to the Safe Drinking Water Act.

A water balance, which identified specific wastewater sources and volumes generated from these sources, was requested for the Catlettsburg refinery. Ashland stated that they did not have information on flows from specific wastewater sources, but did provide a very general facility water balance [Appendix D].

Process wastewaters are discharged to either the facility oily water sewer or the newer benzene sewer. Wastewaters with high benzene concentrations are segregated and pumped to the benzene recovery unit (BRU), prior to being

further treated in the main wastewater treatment plant. In addition to refinery process wastewater, Ashland has installed approximately 30 groundwater recovery wells, to capture hydrocarbon-contaminated groundwater, and this wastewater is also directed to the BRU. The benzene sewer and treatment unit were installed to meet Clean Air Act National Emission Standards for Hazardous Air Pollutants (NESHAPs) Subpart FF requirements. All other wastewater streams, including contaminated stormwater, are discharged to the oily water sewer, which goes directly to the main wastewater treatment facility. Sewer diagrams were available for the benzene NESHAPs sewer; however, Ashland stated that they are currently in the process of developing sewer diagrams for the older oily water sewer.

Sanitary wastewater is treated in individual package treatment plants located throughout the facility. Effluent from these units is then directed to the oily water sewer for further treatment in the main wastewater treatment facility. As previously discussed, the package treatment plant at the old H-Coal facility is authorized to discharge directly to the Big Sandy River. There are some remote areas of the plant, where sanitary wastewater is diverted to holding tanks. These holding tanks are pumped out and receive treatment at a local publicly owned treatment works.

WASTEWATER TREATMENT

Main Wastewater Treatment Plant

The Ashland main wastewater treatment plant (WWTP) consists of gravity oil-water separation, dissolved air flotation, biological treatment, and clarification. A schematic of the Ashland WWTP is presented in Figure 1.

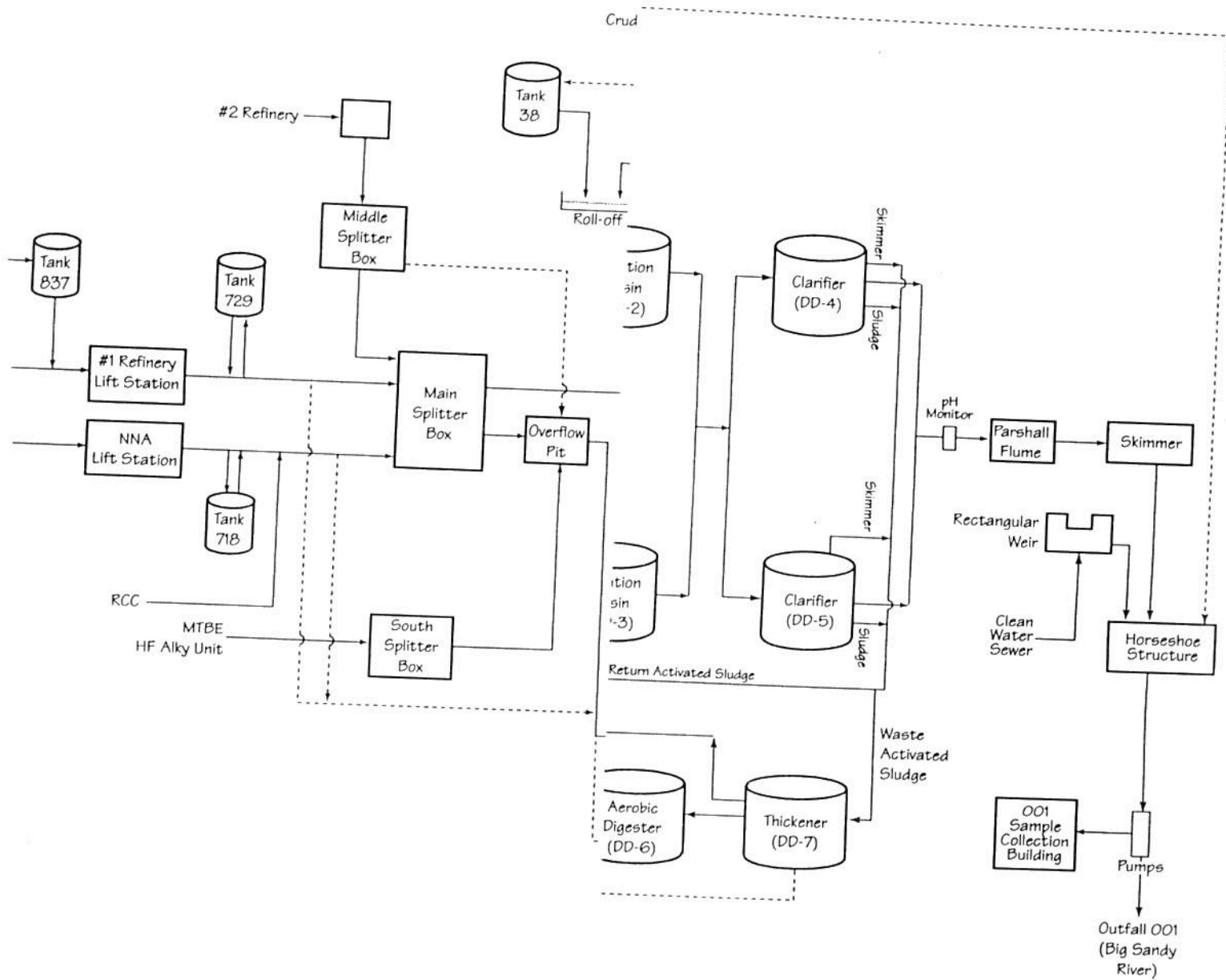


Figure 1
 WATER TREATMENT PLANT SCHEMATIC
 Ashland Petroleum Company
 Catlettsburg, Kentucky

Wastewater from the oily water sewer enters the main wastewater treatment plant at three splitter boxes. The wastewater from the number 2 refinery enters the middle splitter, where it normally flows to the main splitter box. High flows to the middle splitter box could be diverted to the overflow pit. Wastewater from the number 1 refinery, the new north area, and the Reduced Crude Conversion (RCC) unit goes directly to the main splitter box. Wastewater from the main splitter box is normally evenly split to three gravity oil-water separators; however, high flows can be diverted to the overflow pit. Wastewater from the MTBE and Alky units is currently directed to the overflow pit. Wastewater entering the overflow pit is pumped to one of the storm/surge tanks (tanks 858 and 822). According to Ashland personnel, wastewater is preferentially directed to surge tank 858 first, because it has a floating roof cover; however, the uncovered surge tank 822 is also used when needed.

Process wastewater is split evenly between three gravity oil-water separators (north, south, and middle separators). All three separators have had covers installed, which is required by Kentucky air quality requirements. The north and south separators have a similar design (single pass basins), with one slotted pipe oil skimmer for collected oil from the top of the unit. The middle separator is a double pass basin, with two slotted pipe oil skimmers. There is also a concrete wall surrounding the middle separator, whereas, no wall surrounds the north and south separators. None of the three separators have operational oil and sludge flights, for directing sludge to a hopper and oil to the slotted pipe skimmers. The flights became inoperable in 1991 and have not been repaired.

Oil collected from the three separators is directed to tank 894. Water draws from this tank are directed to the BRU, whereas the oil is pumped to

crude storage tanks. Due to the inoperable flights, the oil-water separators must be taken out of service in order to remove sludge. After dewatering the separators, sludge is pumped to roll-offs and the sludge is further processed prior to off-site disposal.

The effluent from the three separators is combined, and the pH of the combined separator effluent can be adjusted by caustic addition. The treatment plant previously had the capability of adding acid; however, the acid feed system has been inoperable for years. Wastewater that has been diverted to the storm/surge tanks is normally discharged to the effluent side of the oil-water separators.

After pH adjustment, the wastewater is pumped to an equalization tank to dampen flow fluctuations. Cationic polymer is then added, and the wastewater split evenly to two dissolved air flotation (DAF) units. DAF float and sludge is pumped to tanks 35 and 36, and directed to the RCC unit via tanks 709 and 717.

DAF effluent can be pumped to a cooling tower during the summer months, to ensure compliance with the 100 °F permit limitation at Outfall 001. Effluent from the BRU is normally combined with DAF effluent; however, operators have the capability of diverting BRU effluent to the influent of the DAF units.

The wastewater is then pumped to two aeration basins, operated in parallel. Phosphoric acid is added to the influent of the aeration basins, to ensure adequate phosphorous concentrations for biological growth. The aeration basins are equipped with three surface aerators; however, only two are normally

used. The effluent from the aeration basins is evenly split between two clarifiers for solids removal. Clarifier sludge is returned to the aeration basin influent to maintain adequate concentrations of biological organisms. Excess sludge is wasted to a gravity thickener. Thickener effluent is then aerobically digested and directed to a sludge holding tank, where it can be pumped (along with DAF float) to tanks 35 and 36 (and potentially tanks 709 and 717), where it is stored prior to use as feed to the RCC unit.

Clarifier effluent is then combined and routed through a parshall flume for flow measurement. Water depth in the parshall flume is measured continuously with a bubbler, and the information transmitted continuously to the Ashland computer system where the flow is calculated and recorded. The effluent then flows through a skimmer (which has a mechanical oil collection arm), and discharges to a basin referred to as the horseshoe structure. The horseshoe structure has a baffle. Wastewater must flow underneath the baffle and free floating oil can be captured. An additional wastewater source, referred to as the clean water sewer, flows into the horseshoe structure. The clean water sewer, consisting primarily of boiler blowdown, flows through a rectangular weir. A bubbler is also used to measure water depth in the weir and this information is also continuously transmitted to the Ashland computer system for flow calculation and recording. There are two 4,000 gpm pumps at the horseshoe structure to pump wastewater to the Big Sandy River through Outfall 001.

Benzene Recovery Unit (BRU)

The Ashland benzene recovery unit (BRU) consists of gravity oil-water separation, equalization, nitrogen stripping, and activated carbon treatment of

the hydrocarbon-contaminated nitrogen stream. A schematic of the Ashland BRU is presented in Figure 2.

Wastewater discharged to the benzene NESHAPs sewer is directed to two corrugated plate interceptors (CPIs) to remove oil. Oil from the two CPIs is pumped to tank 894 (along with oil from the three oil-water separators at the main WWTP), prior to being pumped back to crude oil storage tanks. CPI effluent is pumped to tank 890, a floating roof tank, for flow equalization.

Wastewater from the equalization tank is then pumped to a stripping tower for benzene recovery. There are two strippers; only one stripper is normally in use and the other in stand-by mode. Each of the strippers is preceded by a basket straining filter to prevent clogging of the column. Nitrogen gas is used in the stripping tower. Wastewater effluent from the stripping tower is normally discharged to the influent of the aeration basins at the main WWTP, but can also be directed to the influent of the DAF units.

The benzene-containing nitrogen gas is then routed to an activated carbon polishing bed which is impregnated with potassium hydroxide. Potassium hydroxide can neutralize any hydrogen sulfide which also may be stripped from the wastewater. The gas is then passed through a dehumidifier, before being directed to a carbon bed adsorber, for benzene recovery. There are two carbon bed adsorbers; one in operational mode and the other in regeneration mode or standby. The carbon bed adsorbers are regenerated daily with superheated steam. The condensed steam is pumped to tanks 35 and 36 (along with DAF float), and eventually processed at the RCC unit. The nitrogen gas is then recirculated to the stripping towers.

ON-SITE INSPECTION SUMMARY

Credentials were presented to Roy Whitt, Plant manager, Catlettsburg Refinery. Following a general discussion of refinery processes, including wastewater treatment, a plant tour was conducted. The following facility areas were inspected: various wastewater generation points, the wastewater treatment systems, outfall monitoring locations, and tank containment structures. Records/documents affiliated with the regulated activity were also reviewed.

Facility Inspection/Discussions

A discussion of major facility areas inspected follows. Included is a brief description of activities and observations noted.

Wastewater Treatment Plant/Outfall 001

The wastewater treatment plant is operated 24 hours per day by a crew consisting of a supervisor and two operators each shift. Monitoring is conducted on internal wastestreams to identify any unusual conditions. [Blank copies of the internal sampling and analysis sheets are contained in Appendix E.]

The results from the internal monitoring conducted is usually available in the afternoon for the morning samples that were collected. However, if there are unusual conditions, this turnaround time is not always sufficient to prevent upsets at the WWTP.

An upset at the WWTP occurred during the NEIC inspection. The WWTP supervisor received notification on October 28, 1996 that a highly acidic, sulfide-containing wastestream was going to be generated from the cleaning of Ijungstrom wheels at the number 5 crude unit. This material was supposed to be directed to tankage within the refinery and drained slowly to the WWTP; however, some of this wastewater was discharged directly to the WWTP. On October 29, 1996, the capacity of the caustic addition system was inadequate and the pH was slightly depressed (7.0 to 7.5) from the normal pH range conditions (8.0 to 9.0) for the aeration basins. The discharge of this sulfide-containing material also resulted in some biological die-off, and the impact of this could readily be seen by poor settling sludge at the clarifiers during the NEIC inspection. EPA Region 4 staff examined the aerobic biomass under a microscope, and were unable to identify microbial organisms such as protozoans or rotifiers, which would normally be present in an activated sludge biomass. Due to the young sludge resulting from the biomass die-off incident, solids were still not settling very well at the clarifier even as of November 6, 1996. Ashland's WWTP does not have pH meters at the API separator inlet; therefore, this low pH material was not detected until after it passed through the separators. Operators then began diverting wastewater to the storm/surge tanks from the main splitter boxes; however, a large slug of this material was already in the system. Wastewater could have been diverted to the WWTP storm/surge tanks earlier, if there was an in-line pH monitor at the WWTP inlet. The oily conditions at the WWTP influent will make it difficult to keep pH monitors working properly, without regular cleaning of the probes. An alternative would be to increase the pumping capacity of the lift station (which follows the separators) to divert wastewater to the storm/surge tanks after it has received treatment through the oil-water separators.

The inability to detect unusual conditions (slug loadings, spills, etc.) at the WWTP quickly enough to divert wastewater to tankage has occurred previously and resulted in permit violations. As an example, during July 1996, amine from a recirculating system leaked and reached the WWTP resulting in a BOD violation. During the same month, high organic wastewater from maintenance activities in the petrochemical area also caused BOD permit limits to be exceeded. Ashland needs to review its internal monitoring program; assess the feasibility of installing in-line monitoring equipment (total organic carbon, pH, etc.); and/or evaluate the need to provide increased capacity to divert wastewater to storm/surge tanks following the oil-water separators.

The three oil-water separators do not have functional chain and flight oil and sludge moving devices. These devices, which have flights that span the width of the separator, move separated oil collected at the top of the unit towards the slotted pipe oil skimmer and sludge collected at the bottom of the unit towards a hopper, where it can be pumped out. Without this equipment, sludge accumulated in the separator cannot be effectively removed without taking the unit out of service. During the beginning of the NEIC inspection, the middle separator was out of service in order to remove accumulated sludge. This unit has been out of service since March 26, 1996. During the inspection, the middle separator was returned to service; however, the south separator was removed from service to initiate sludge removal from this unit. Each of the separators has a design capacity of 2,000 gpm. With one unit out of service, the separators are at or exceeding design capacity for average flow conditions. Without operable flights, these units can not be expected to efficiently operate at design capacity for long periods of time. Ten to twelve rollofs of sludge were removed from the middle separator, with almost 5 feet of sludge accumulated in the unit when it was removed from service. These units cannot be expected

to operate at design capacity with the effective depth of the unit significantly reduced by accumulated sludge. Free oil was observed floating on top of the equalization tank, which follows the oil-water separators [Photograph 1]. Failure to adequately remove free floating oil could impact the performance of the downstream units, particularly the activated sludge treatment.

The WWTP was designed to provide pH adjustment capacity. Currently, Ashland has the ability to add caustic soda, in order to raise pH levels. However, the acid feed pumps at the WWTP have been inoperable for a number of years. As the refinery has numerous high pH wastewater sources including caustic scrubbers, it is possible that alkaline wastewater could be spilled into the refinery sewers. Without the capacity to neutralize high pH wastewater with acid addition, the only alternative to the operators would be to divert this material to the surge tanks, and slowly feed it to the WWTP to prevent any permit violations. Acid addition capability would also allow operators to adjust pH conditions to optimize biological treatment efficiency.

Flow discharged from the WWTP is measured at a parshall flume, which is located downstream of the clarifiers. The depth of the water in the clarifier is measured continuously with a bubbler system. The bubbler system readings are fed directly to Ashland's Utilities computer (ARTIS), where instantaneous flow values are calculated, and a totalized flow is recorded every day. On October 31, 1996, there were high flows at the treatment plant, and it was noted, that there was turbulence at the parshall flume inlet. Turbulence can effect the height measurements and ultimately the flow values. During other periods that the parshall flume was observed, flows were not high and no turbulent conditions were noted. Therefore, during high flow periods, flow

measurements are likely to have a greater degree of error. Dry weather flows measured at the parshall flume average approximately 4,000 gpm.

Another wastewater source, referred to as the clean water sewer, is combined with WWTP effluent at the horseshoe structure prior to discharge at Outfall 001. The primary wastewater source discharged to the clean water sewer is boiler blowdown. Flow is measured from the clean water source at a rectangular weir located just prior to the horseshoe structure. The depth of the water at the weir is measured continuously with a bubbler system. The bubbler system readings are fed directly to Ashland's Utilities computer (ARTIS), where instantaneous flow values are calculated and a totalized flow is recorded every day. The totalizer readings, from the parshall flume and rectangular weir, are added together to calculate the total flow discharged through Outfall 001. Flow from the clean water sewer had been averaging approximately 500 gpm, but some sources have been eliminated and/or diverted, reducing the flow to approximately 300 gpm.

Ashland personnel check the calibration of the flow monitoring devices at the WWTP (both the parshall flume and rectangular weir) on a weekly basis. Any problems are reportedly immediately corrected. Bubbler adjustments that are made during the calibration check should be recorded by Ashland personnel, but no records were maintained on flow measurement equipment adjustments.

An automatic refrigerated sampler is used to collect time composited effluent samples prior to discharge to the Big Sandy River from Outfall 001. From the pumps located at the horseshoe structure, which discharge to the Big Sandy River, a small constant flow is continuously directed to the composite sampler. The NPDES permit has monitoring requirements for some parameters

that require 24-hour composite samples; however, the permit does not specify whether the 24-hour composite sample should be time or flow proportional. According to Kentucky Administrative Regulations (KAR), Title 401, Section 5:050 (50):

“Twenty-four (24) hour composite sample” means not less than twelve (12) effluent portions collected at regular intervals over a period of twenty-four (24) hours which are composited in proportion to flow;

Therefore, 24-hour composite samples are not being collected (flow-composited) in accordance with applicable state regulations.

Oil and grease grab samples are being collected at Outfall 001 from the tygon tubing that directs a small flow from the effluent pumps to the refrigerated sampler. Oil and grease samples should not be collected through tygon tubing, as oil could be absorbed/desorbed from the tubing. Additionally, grab samples collected for temperature and pH are not being measured by field personnel, but are taken back to the laboratory. In accordance to 40 CFR Part 136, temperature and pH samples are required to be analyzed immediately (which is defined as within 15 minutes). It is possible that these samples could be analyzed within the required time frame if they are immediately driven back to the lab and analyzed; however, having pH and temperature samples analyzed by the sampling technician would ensure that this occurs. Alternatively, monitoring requirements could be changed to require continuous monitoring with a pH meter and temperature thermocouple, as Outfall 001 is the major discharge point for the refinery.

DAF float and waste activated sludge was previously dewatered in filter presses and shipped off-site for disposal; however, this material is now combined

and reprocessed in the RCC unit of the refinery. Waste activated sludge is first thickened and digested prior to being reprocessed. A spill from the skimming/scum box of the sludge thickening tank (tank DD7) had recently occurred [Photograph 2].

Benzene Recovery Unit (BRU)

The BRU was designed to achieve an annual average benzene effluent concentration of less than 10 mg/L. This unit has not achieved the design goals for benzene treatment, as outlined in the Clean Air Act, Subpart FF report. One of the factors for the higher benzene effluents levels is the BRU design did not adequately account for the benzene loading from extraction wells, which have been installed for groundwater remediation purposes. Ashland is planning on constructing two additional stripping columns, doubling the BRU capacity. If the unit is still unable to meet benzene treatment goals, then other modifications may be necessary.

Nonprocess Wastewater Outfalls

All potentially contaminated stormwater is discharged to the oily water sewer and treated at the WWTP. Noncontaminated stormwater and nonprocess wastewaters (such as boiler blowdown, and occasionally hydrostatic test waters) are authorized to be discharged through permitted outfalls, as described in Appendix B. During the NEIC inspection, these nonprocess outfalls were inspected on two occasions during minor rainfall events. For the outfalls that had a stormwater discharge, no visible oil and grease was noted during the inspections. Many of these nonprocess outfalls have no flow measurement equipment, and the flow information reported on the DMRs are very rough

estimates. On November 1, 1996, it was observed that an oil soaked adsorbent pad had been discarded adjacent to outfall 022 [Photograph 3]. During an inspection of outfall 020 on November 4, 1996, it was observed that there is a diesel product seeping below a concrete pad, located southeast of the North Product tank farm [Photograph 4]. Above the concrete pad there were a couple of pumps and an oil-water separator, which can be used to treat stormwater from the diked tank farm area. The concrete pad is adjacent to a drainage ditch, which outfall 020 discharges to a few yards to the south. Ashland personnel could not determine what the source of the oil was below this concrete pad.

On November 4, 1996, the upper lake (which discharges to Outfall 006) was inspected. Discharges from the boiler house (blowdown, filter and ion exchange backwash water) enter the upper lake in the southwest corner, and are generally above the permitted pH range (6.0 to 9.0) for Outfall 006. In order to adjust pH values, sulfuric acid is dripped into the lake at the northwest corner. No mixing equipment is provided, and the sulfuric acid addition is only adjusted manually once per shift. The pH adjustment equipment and procedures are not adequate to ensure compliance with permit requirements, and a number of permit violations have occurred. Until improvements to the pH adjustment system are made, it is recommended that the discharge point from the upper lake be equipped with a continuously recording pH meter with alarms, to immediately notify WWTP operators of any discharges outside of the permitted pH range. The upper lake is also very vulnerable to spills, due to its location within the refinery. There was a skimming device located at the outlet of this waterbody; however, this equipment is no longer functional. Spill records indicate that a major spill (50 barrels) to the upper lake last occurred in January 1994.

Sanitary wastewater (Internal outfalls)

Sanitary wastewater is segregated and treated in automated package treatment plants located throughout the refinery. No concerns with this equipment were noted during the inspection. Effluent from these units receive further treatment in the main WWTP. In addition to the package treatment plants, there are some portable bathroom facilities and holding tanks at remote areas of the refinery that do not have access to the sanitary sewer line. This wastewater is pumped out by vacuum truck and discharged to the local publicly owned treatment works.

Oil Containment Structures

During the NEIC inspection, a number of tank farms were inspected including the crude tank farm, RCC tank farm, north tank farm, Viney branch tank farm, and the north area product tank farm. Valves for secondary containment structures, which allow the discharge of accumulated stormwater to NPDES permitted outfalls, valves were kept in a closed position. For secondary containment structures drains that discharge to Ashland's sewer system, valves were left in an open position even during dry weather conditions. If a tank were to overflow or a catastrophic failure were to occur, oil could easily overload Ashland's wastewater treatment facilities. A complete inventory was conducted by Ashland, and it was determined that 33 drain valves from tank farm containment structures to the oily water sewer were in the open position. An additional 6 drain valves from tank farm containment structures, which direct stormwater to the NESHAPS sewer, were in the open position. Ashland personnel closed these valves during the NEIC inspection. A Standard Operation Procedure (SOP) for the draining of stormwater from tank farm

containment structures was requested but not provided by Ashland. Specific procedures for draining stormwater from these containment structures need to be developed.

In 1994, Ashland hired a contractor to assess the adequacy of their secondary containment structures at the refinery. A report (referred to as the volumetric capacity study) was prepared, which identified areas with inadequate secondary containment capacity. Corrections to all the deficiencies noted in the study were not completed before the contract ended. Completion of this work was to be done by Ashland personnel; however, some of this work has not been completed. The contractor identified the following containment areas (CA) which needed additional capacity: CA-1, CA-9, CA-27, CA-28, CA-30, CA-43. Ashland environmental staff believed that some of these projects (CA-9, CA-27, CA-28, and CA-43) have been completed, but this information was not confirmed.

During the inspection, numerous stained soil areas were identified, indicating spills to the environment. Stained soil near a diesel dye additive container, containing xylene, was observed outside a containment pad for the pumps at the North Product Tank Farm [Photograph 5]. Stained soil was identified under pipeline trestles in the North tank farm [Photograph 6]. The spill occurred when an oily water sewer pump (adjacent to tank 790) failed. The entire area, which was within an earthen secondary containment area, was flooded with oily wastewater. A bobcat was brought in to clean the soil; however, the soil under the trestle was not removed. Stained soil was also identified near a sump adjacent to tank 812. On November 1, 1996, a pipeline control valve was leaking heavy cycle oil to the ground [Photograph 7]. This

material was draining to a nearby oily water sewer drain. These examples are indicative of poor housekeeping practices within the refinery.

Water draws from oil storage tanks are hard piped to either the oily water or NESHAPs sewer, depending upon the benzene concentration of the stored material and the proximity to the sewer lines. Up until the effective date of the new TCLP standard for benzene under RCRA, water draws from the crude tank farm were discharged to an earthen impoundment area referred to as the crude pond [Photograph 8]. Ashland personnel stated that no discharges have occurred to the crude pond after the effective date of the benzene TCLP regulation. No clean-up of the crude pond has been undertaken.

Records/Document Review

Effluent Guideline Characterization

NEIC conducted a review of process information in order to verify Ashland's categorization as an integrated refinery, as defined in 40 CFR § 419.50. Based on Ashland's process description, it was confirmed that the refinery produces petrochemical products by the use of topping, cracking, and lube oil manufacturing. Therefore, in order to be classified as an integrated refinery, it was only necessary to document that Ashland is also a petrochemical operation, as defined in 40 CFR § 419.31. In order to be classified as a petrochemical operation, Ashland must manufacture second-generation petrochemicals or first-generation petrochemicals when 15% or more of refinery production is as first-generation petrochemicals and isomerization products. Ashland does produce second-generation petrochemicals, including cumene and MTBE; therefore, it was not necessary to quantify the percentage of first

generation chemicals produced. Ashland is correctly categorized as an integrated refinery.

The basis for the categorical permit limitations was the estimated production capacity for the refinery process units which was provided in Ashland's permit application. In accordance with 40 CFR § 122.45(b)(2), permit limits based on production should be based upon a reasonable measure of actual production of the facility and not production capacity. Therefore, Ashland did not provide the proper production information in their permit application, as required by 40 CFR § 122.21(g)(5). The use of actual production figures would have reduced the permit limitations included in Ashland's permit. Actual FY96 production versus design production is compared below.

<u>Process Unit</u>	<u>Design Capacity</u>	<u>FY96 Production</u>
Atm. Crude Distillation	245,000 bbl/day	216,804 bbl/day
Vac. Crude Distillation	60,000 bbl/day	38,506 bbl/day
Desalting	245,000 bbl/day	216,804 bbl/day
Cracking	117,000 bbl/day	85,447 bbl/day
Hydrotreating	232,500 bbl/day	149,442 bbl/day
Reforming	53,000 bbl/day	38,388 bbl/day
Asphalt	65,000 bbl/day	17,810 bbl/day
Lube	100,500 bbl/day	62,394 bbl/day
Cumene	6,000 bbl/day	4,000 bbl/day

Discharge Monitoring Reports

Discharge monitoring reports (DMRs) for the period of January 1994 to September 1996 were reviewed. Table 1 summarizes the exceedances of effluent limitations at the permitted outfalls. DMRs document 39 daily maximum and 12 monthly average exceedances for Outfall 001, 2 daily maximum exceedances

Table 1

EXCEEDANCES OF NPDES PERMIT LIMITATIONS
Ashland Petroleum Company
Catlettsburg, Kentucky

Date	Outfall	Parameter	Permit Limit ¹	Value Reported
11/07/96	001	Toxicity	3.75 Tu _a	>16.7 Tu _a Ceriodaphnia
10/23/96	001	Toxicity	3.75 Tu _a	12.5 Tu _a Ceriodaphnia
10/11/96	001	Toxicity	3.75 Tu _a	5.9 Tu _a Ceriodaphnia
9/26/96	001	Toxicity	3.75 Tu _a	5.9 Tu _a Ceriodaphnia
9/30/96	006	pH	6.0 - 9.0 SU	9.6 SU
9/26/96	016	TSS	45 mg/l (DM)	50 mg/l
September 96	016	TSS	30 mg/l (MA)	50 mg/l
3rd quarter 96 (9/11-12/96)	001	Toxicity	3.75 Tu _a	>16.7 Tu _a Ceriodaphnia
8/28/96	001	Phenol	110.4 lbs/day (DM)	150.3 lbs/day
7/15/96	001	BOD	12,665 lbs/day (DM)	9,632 lbs/day
7/10/96	001	BOD	15,156 lbs/day (DM)	9,632 lbs/day
7/30/96	006	pH	6.0 - 9.0 SU	9.2 SU
7/30/96	006	Chloride	1,220 mg/l (DM)	2,440 mg/l
7/18/96	011	pH	6.0 - 9.0 SU	4.4 SU
July 96	001	BOD	5,126 lbs/day (MA)	5,745 lbs/day
July 96	006	Temperature	96° F (MA)	95° F
June 96	001	BOD	5,126 lbs/day (MA)	5,803 lbs/day
2nd quarter 96 (6/25/96)	001	Toxicity	2.38 Tu _a	14.3 Tu _a Daphnia pulex

Table 1 (continued)

Date	Outfall	Parameter	Permit Limit ¹	Value Reported
4/18/96	001	Cyanide	0.136 mg/l (DM)	0.260 mg/l
3/12/96	001	TSS	8,768 lbs/day (DM)	6,631 lbs/day
3/28/96	006	pH	6.0 - 9.0 SU	9.2 SU
3/21/96	016	TSS	45 mg/l (DM)	56 mg/l
March 96	016	TSS	30 mg/l (MA)	56 mg/l
March 96	016	BOD	30 mg/l (MA)	34 mg/l
2/8/96	001	BOD	9,632 lbs/day (DM)	23,635 lbs/day
2/8/96	015	Oil and grease	15 mg/l (DM)	30.8 mg/l
2/8/96	016	TSS	45 mg/l (MA)	80 mg/l
2/22/96	017	pH	6.0 - 9.0 SU	5.7 SU
February 96	001	BOD	5,126 lbs/day (MA)	5,758 lbs/day
February 96	001	Cyanide	0.04 mg/l (MA)	0.078 mg/l
February 96	016	TSS	30 mg/l (MA)	80 mg/l
February 96	016	BOD	30 mg/l (MA)	40 mg/l
1/31/96	005	Oil and grease	15 mg/l (DM)	143.9 mg/l
1/2/96	006	pH	6.0 - 9.0 SU	9.3 SU
January 96	016	TSS	30 mg/l (MA)	40 mg/l
December 95	001	Cyanide	0.04 mg/l (MA)	0.05 mg/l
4th quarter 95 (12/18/95)	001	Toxicity	2.38 Tu _a	6.7 Tu _a Daphnia pulex
11/7/95	001	BOD	9,632 lbs/day (DM)	10,914 lbs/day
9/12/95	023	Oil and grease	15 mg/l (DM)	16.3 mg/l
3rd quarter 95 (9/27/95)	001	Toxicity	2.38 Tu _a	4.5 Tu _a Daphnia pulex

Table 1 (continued)

Date	Outfall	Parameter	Permit Limit ¹	Value Reported
8/25/95	001	TSS	6,631 lbs/day (DM)	6,902 lbs/day
8/30/95	010	Fecal coliform	400/100 ml (7DG)	>6000/100 ml
8/30/95	019	Fecal coliform	400/100 ml (7DG)	1500/100 ml
August 95	006	Temperature	96° F (MA)	95° F
August 95	006	Zinc	0.5 mg/l (MA)	0.62 mg/l
August 95	010	Fecal coliform	200/100 ml (30DG)	>6000/100 ml
August 95	019	Fecal coliform	200/100 ml (30DG)	1500/100 ml
7/10/95	001	Cyanide	0.136 mg/l (DM)	0.389 mg/l
7/13/95	012	pH	6.0 - 9.0 SU	9.3
July 95	001	Cyanide	0.04 mg/l (MA)	0.389 mg/l
July 95	016	TSS	30 mg/l (MA)	40 mg/l
6/22/95	006	Zinc	1.0 mg/l (DM)	1.9 mg/l
6/1/95	015	pH	6.0 - 9.0 SU	9.4 SU
June 95	006	Zinc	0.5 mg/l (MA)	1.9 mg/l
5/19/95	001	TSS	6,631lbs/day (DM)	12,173 lbs/day
5/2/95	001	TSS	6,631lbs/day (DM)	8,606 lbs/day
5/19/95	001	Phenol	93.42 lbs/day (DM)	167.7 lbs/day
5/15/95	015	pH	6.0 - 9.0 SU	9.7 SU
May 95	001	Cyanide	0.04 mg/l (MA)	0.06 mg/l
May 95	016	TSS	30 mg/l (MA)	35 mg/l
4/19/95	018	Fecal coliform	400/100 ml (7DG)	610/100 ml
3/16/95	011	Fecal coliform	400/100 ml (7DG)	>6000/100 ml
3/16/95	013	Fecal coliform	400/100 ml (7DG)	2700/100 ml

Table 1 (continued)

Date	Outfall	Parameter	Permit Limit ¹	Value Reported
3/30/95	024	Fecal coliform	400/100 ml (7DG)	1900/100 ml
March 95	024	Fecal coliform	200/100 ml (30DG)	1900/100 ml
1/24/95	001	TSS	6,631 lbs/day (DM)	7,641 lbs/day
1/25/95	018	Fecal coliform	400/100 ml (7DG)	>6000/100 ml
1/16/95	001	TSS	6,631 lbs/day (DM)	11,847 lbs/day
December 94	012	Fecal coliform	200/100 ml (30DG)	340/100 ml
December 94	016	TSS	30 mg/l (MA)	34 mg/l
10/26/94	008	Fecal coliform	400/100 ml (7DG)	1400/100 ml
10/26/94	016	Fecal coliform	400/100 ml (7DG)	1800/100 ml
10/12/94	024	Fecal coliform	400/100 ml (7DG)	2700/100 ml
8/30/94	006	pH	6.0 - 9.0 SU	9.1
8/30/94	013	Fecal coliform	400/100 ml (7DG)	>6000/100 ml
8/31/94	019	Fecal coliform	400/100 ml (7DG)	5639/100 ml
8/31/94	023	Oil and grease	15 mg/l (DM)	25.2 mg/l
8/30/94	024	Fecal coliform	400/100 ml (7DG)	470/100 ml
August 94	013	Fecal coliform	200/100 ml (30DG)	>6000/100 ml
August 94	019	Fecal coliform	200/100 ml (30DG)	5300/100 ml
7/19/94	008	pH	6.0 - 9.0 SU	10.6
6/1/94	001	BOD	9,632 lbs/day (DM)	19,502 lbs/day
6/16/94	012	pH	6.0 - 9.0 SU	9.3
4/6/94	001	TSS	6,631 lbs/day (DM)	11,606 lbs/day
4/6/94	001	Hex. Chromium	5.25 lbs/day (DM)	7.15 lbs/day

Table 1 (continued)

Date	Outfall	Parameter	Permit Limit ¹	Value Reported
4/25/94	006	pH	6.0 - 9.0 SU	9.2
4/29/94	007	Oil and grease	15 mg/l (DM)	61 mg/l
3/9/94	001	BOD	9,632 lbs/day (DM)	10,484 lbs/day
3/9/94	001	Oil and grease	3,010 lbs/day (DM)	22,201 lbs/day
3/16/94	005	Oil and grease	15 mg/l (DM)	23.7 mg/l
3/17/94	017	pH	6.0 - 9.0 SU	9.3
3/17/94	017	Fecal coliform	400/100 ml (7DG)	>6000/100 ml
March 94	001	Oil and grease	1,604 lbs/day (MA)	2,077 lbs/day
March 94	016	Fecal coliform	200/100 ml (30DG)	350/100 ml
1st quarter 94 (3/8/94)	001	Toxicity	2.38 Tu _a	5.6 Tu _a Daphnia pulex
2/3/94	001	BOD	9,632 lbs/day (DM)	10,821 lbs/day
2/2/94	001	BOD	9,632 lbs/day (DM)	14,429 lbs/day
2/1/94	001	BOD	9,632 lbs/day (DM)	14,188 lbs/day
2/23/94	001	TSS	6,631 lbs/day (DM)	12,899 lbs/day
2/10/94	001	TSS	6,631 lbs/day (DM)	6,823 lbs/day
2/9/94	001	TSS	6,631 lbs/day (DM)	17,648 lbs/day
2/14/94	001	Cyanide	0.136 mg/l (DM)	0.553 mg/l
2/8/94	017	pH	6.0 - 9.0 SU	9.6 SU
February 94	001	TSS	4,222 lbs/day (MA)	4,566 lbs/day
February 94	001	Cyanide	0.04 mg/l (MA)	0.282 mg/l

Table 1 (continued)

Date	Outfall	Parameter	Permit Limit ¹	Value Reported
1/21/94	001	BOD	9,632 lbs/day (DM)	18,128 lbs/day
1/21/94	001	pH	6.0 - 9.0 SU	9.2 SU
1/27/94	001	TSS	6,631 lbs/day (DM)	8,070 lbs/day
1/27/94	001	Zinc	0.764 mg/l (DM)	0.77 mg/l
1/26/94	008	pH	6.0 - 9.0 SU	5.4 SU
1/26/94	019	pH	6.0 - 9.0 SU	5.9 SU
1/25/94	018	Fecal coliform	400/100 ml (7DG)	>6000/100 ml
1/31/94	024	Fecal coliform	400/100 ml (7DG)	530/100 ml
January 94	001	BOD	5,126 lbs/day (MA)	5,130 lbs/day
January 94	001	Zinc	0.5 mg/l (MA)	0.77 mg/l
January 94	024	Fecal coliform	200/100 ml (30DG)	530/100 ml

¹ All daily maximum limits are indicated by a DM, whereas monthly average limits are indicated by an MA. The fecal coliform limits are 7 day geometric mean (7DG) and 30 day geometric mean (30DG). pH limits are instantaneous. Acute toxicity limits are indicated by the symbol Tu_a (100/LC50).

for Outfall 005, 8 daily maximum and 4 monthly average exceedances for Outfall 006, 1 daily maximum exceedance for Outfall 007, 3 daily maximum exceedances for Outfall 008, 1 daily maximum and 1 monthly average exceedance for Outfall 010, 2 daily maximum exceedances for Outfall 011, 2 daily maximum and 1 monthly average exceedance for Outfall 012, 2 daily maximum and 1 monthly average exceedance for Outfall 013, 3 daily maximum exceedances for Outfall 015, 4 daily maximum and 10 monthly average exceedances for Outfall 016, 4 daily maximum exceedances for Outfall 017, 2 daily maximum exceedances for Outfall 018, 3 daily maximum and 2 monthly average exceedances for Outfall 019, 2 daily maximum exceedances for Outfall 023, and 4 daily maximum and 2 monthly average exceedances for Outfall 024 during the time period between January 1994 through October 1996. It should be noted that the monthly average and daily maximum limits established for fecal coliform are defined in the permit as 30-day and 7-day geometric means.

KYDEP assessed an \$8,000 penalty for violations of the cyanide limit at Outfall 001 for May, July, and December 1995 and February 1996, and for TSS violations at Outfall 016 for February and March 1996 [Appendix F].

A review of the DMRs also identified areas of noncompliance with the NPDES monitoring requirements. Ashland failed to conduct the required monitoring for pH, temperature, oil and grease, total organic carbon, chloride, and zinc at Outfall 006 during the month of December 1995. Ashland failed to conduct the required monitoring for TSS and TOC at outfall 023 during June 1994. Ashland failed to conduct the required monitoring for TSS at Outfall 007 for May 1994.

Due to heavy rainfall, Ashland discharged approximately 2,500 gpm of DAF effluent directly to the Big Sandy River (bypassing biological treatment) via Outfall 001 from 05:00 on May 16, 1996 to 13:00 on May 17, 1996. Due to heavy rainfall, Ashland discharged DAF effluent directly to the Big Sandy River (bypassing biological treatment) via Outfall 001 from 11:00 May 18, 1995 to 08:30 on May 19, 1995. Part II of Ashland's NPDES permit subjects the permittee to the standard permit conditions contained in KAR, Title 401, 5:065 Section 1. Section (13)(d) of this regulation prohibits bypassing unless it is unavoidable to prevent loss of life, personal injury or sever property damage, there were no feasible alternatives, and the permittee submits proper notification. As these bypasses were made to prevent severe flooding, and proper notifications were made, they do not violate the bypass prohibition.

Since spring 1993, Ashland has been diverting oily wastewater from the MTBE and HF Alky units to the storm surge tanks, and then discharging this material to the DAF units, bypassing the oil-water separators. This diversion to tankage was made to provide pH equalization of these wastestreams, however, no piping changes were made to allow this wastewater to be pumped back to the WWTP headworks. Stormwater is normally discharged to the DAF units and due to the small amount of free oil associated with this wastestream, this is appropriate. However, MTBE and HF Alky wastewater can contain significant free oil and should receive treatment in the API separators. During the inspection, significant free oil was observed at the equalization tank. As this bypass does not meet the above conditions for allowable bypass and no state notifications were made of this operational change, NEIC concludes that this is a prohibited bypass. In a January 29, 1997 letter to NEIC [Appendix K], Ashland contended that the surge tanks provide equivalent oil-removal treatment as the API separators, thus the use of the surge tank for pH

equalization and oil-removal in lieu of the API separator did not represent a bypass but a prudent use of different components to provide more effective over-all wastewater treatment. Since Ashland concludes that bypasses did not occur, no notification was required. The surge tank was designed to provide flow equalization and not oil-removal. While some oil removal occurs, it is not equivalent treatment, and Ashland could have diverted this wastewater back to the API units by modifying their WWTP piping.

Part D, Section 3 of the NPDES permit requires that Ashland submit a toxicity reduction evaluation (TRE) plan if two consecutive tests exceed permitted levels. Ashland exceeded toxicity limits during two consecutive quarterly samples in 1995: third quarter (September 27 - 28) and fourth quarter (December 18 - 19). On January 29, 1996, KYDEP notified Ashland that they were required to submit a TRE plan within 30 days. Ashland submitted a TRE plan and schedule on February 29, 1996 [Appendix G]. The TRE plan was not approved by KYDEP until August 15, 1996. Phase 1 of the TRE (accelerated testing) was initiated September 26, 1996. [A quarterly sample was also taken September 11, 1996 in accordance with permit requirements]. The first four tests conducted (September 26, 1996; October 11, 1996; October 23, 1996; and November 7, 1996) exceeded permitted toxicity limits by greater than 1.2 times. Ashland's approved TRE requires them to proceed to Phase 2 if they fail four of the six tests, or if two texts exceed the permitted toxicity limits by greater than 1.2 times. Ashland has failed both of these conditions, and must, therefore proceed to Phase 2 of the TRE, which requires Ashland to review WWTP operations.

In addition to conducting the required NPDES permit toxicity tests, Ashland has also been conducting daily in-house acute bioassay testing. Ten

fathead minnows, less than 14 days old, are placed in 100% refinery effluent for intervals between 1 and 4 days. The percent survival rate at the end of the test is recorded. This testing has been conducted for a number of years. Ninety-six (96) hour percent survival rates for the in-house fathead minnow tests, for the last 12 months, are presented in Appendix H. While this data cannot be compared to the toxicity limits in the permit, the data does indicate that Ashland's effluent exhibits variable toxicity. Based upon this data, it does not appear that quarterly toxicity sampling adequately assessed toxicity conditions at this facility. Therefore, the Phase 1 accelerated testing (conducted every 2 weeks) should be maintained throughout the entire TRE. Another concern with the current permitted toxicity monitoring frequency is the potential for Ashland to be able to schedule these quarterly samples only during optimal conditions at the refinery WWTP (i.e., in-house minnow toxicity testing showing no toxicity). Additionally, toxicity testing can be scheduled during periods where no turnarounds or maintenance activities are occurring, when more high strength and potentially toxic wastestreams are generated.

The current permit requires two samples, collected approximately 12 hours apart, be collected and analyzed for toxicity. Based upon a review of the results, the data does not indicate that toxicity is that variable over the 12-hour period. If accelerated testing remains in place, it may not be warranted to require two samples per test.

During interviews of the current and previous WWTP supervisors, NEIC was informed that a TRE was previously conducted by Ashland in the late 1980s/early 1990s. The studies conducted during this previous TRE were requested for review. Only TRE progress reports and a treatability study were provided. Toxicity identification evaluations prepared during the first TRE,

could not be located by Ashland. The Phase 2 progress report stated that a detailed set of oily sewer drawings was being developed, however, this information was not made available.

Ashland has not taken a very proactive response to addressing toxicity problems at the refinery. Ashland environmental management had not assigned a staff person to coordinate TRE activities as of November 1996, even though they had failed their second consecutive quarterly toxicity test in December 1995. The current TRE plan is very general, and specific tasks that will be conducted need to be developed. The TRE plan appears to be starting from ground zero, without utilizing information gained from previous studies. After delaying initiation of Phase 1 of the TRE (awaiting state approval), no planning has been undertaken for initiating future phases of the TRE. Based on the Phase 1 results, Ashland will be required to conduct Phase 2 of the TRE. The current TRE plan is scheduled in incremental phases, with treatability studies (phase 4) not scheduled for at least a year (following completion of phases 2 and 3). Past studies conducted by Ashland have determined that toxicity is primarily caused by an organic fraction (specific toxicants were not identified). Ashland has previously demonstrated that making operational changes at the treatment plant and refinery can reduce toxicity, however, the two consecutive 1995 quarterly compliance samples permit violations, and four consecutive Phase 1 TRE compliance sample permit violations, indicate that toxicity will not be consistently eliminated by operational changes alone. Ashland's in-house toxicity sampling results provide supporting data indicating that the current toxicity problems are not an anomaly. In addition, Ashland exceeded its toxicity limit in the first quarter of 1994. The second quarter 1994 test also exceeded toxicity limits, but was invalidated due to high control mortality (85% survival). Retesting of another sample was in compliance; therefore, a TRE was not

required at that time, but again indicates an inability to prevent toxicity violations with the current procedures and treatment facilities.

Due to the fact that this is Ashland's second TRE, and the existing data indicate an inability to eliminate toxicity through operational changes alone, NEIC recommends that treatability studies be initiated concurrently with Phase 2. Ashland should start by conducting testing to verify their previous findings that the source of toxicity is in the organic fraction. The previous treatability study concluded that expansion of the existing biological treatment plant was infeasible due to site constraints; therefore, future treatability studies should be focused on alternatives that can be easily implemented. Toxicity reduction has been successfully accomplished using activated carbon treatment at other refineries (including other Ashland facilities). Therefore, treatability studies for reducing toxicity (that include powdered and granular activated carbon) should not be delayed, in the event that toxicity cannot be consistently eliminated at Ashland with operational changes alone.

SPCC Records

The discharge of oil in harmful quantities (defined in 40 CFR § 110.3, as violating water quality standards or causing a visible film or sheen on the surface or sludge or emulsion below the surface or upon shoreline) into waters of the United States is prohibited in accordance with 40 CFR § 110.9. Section 4 of Ashland's current SPCC Plan (Spill History) contains summary sheets describing individual spill events at the refinery which violated this prohibition, and were reported in accordance with 40 CFR § 110.10. Table 2 contains a tabulated summary of these spill incidents. Ashland has discharged oil in

harmful quantities to waters of the United States in violation of this regulation on 15 occasions from January 1994 to June 1996.

Ashland's current SPCC plan was certified on October 1, 1996. The previous SPCC plan was certified on March 17, 1994. In accordance with 40 CFR § 112.4 (a), a revised SPCC plan must be submitted within 60 days following two reportable spill events within a 12-month period. As more than two reportable spill events occurred after March 17, 1994 [spills were reported on June 7, 1994; June 15, 1994; July 14, 1994; and June 11, 1995], and the SPCC plan was not revised within 60 days, Ashland has not complied with this requirement.

Storage tanks are scheduled every 5 years for an external integrity inspection and every 20 years for an internal integrity inspection. Dates of the last inspection and next scheduled inspection were requested and are tabulated in Appendix I. Tank inspection records provided by Ashland document that some internal and external tank inspections have not been completed in accordance with this schedule.

Table 2

OIL SPILL SUMMARY
Ashland Petroleum Company
Cattlettsburg, Kentucky

Date	Amount Spilled	Amount Reaching Water	Receiving Water	Cause of Spill
05/31/96	1/2 gallon (approx.)	1/2 gallon	Big Sandy River	Hydrocarbon material leaked from a pipeline flange located on the river bank. The material came from an old abandon asphalt line.
05/16/96	5 gallons	5 gallons	Big Sandy River	Due to the extreme flooding in the area, caused from a large amount of rainfall, the WWT P was bypassed to the Big Sandy River. During the bypass, a sheen of oil and biosolids were noticed near the base of the air assisted flare.
01/03/96	3,000 barrels	2 to 4 barrels	Big Sandy River	Tank 106, fuel oil storage, ruptured near cone roof; suspect moisture entering tank causing expansion.
06/11/95	Very small	Very small	Big Sandy River	Sheen may have resulted from heavy rainfall which caused a fluctuation in interplant lake's level.
07/14/94	1 gallon	1 gallon	Chadwick's Creek	Small spill of light weight lubricating oil.
06/15/94	Unknown	Unknown	Chadwick's Creek	Reoccurrence of electrical conduit oil from 03/09/94 spill.
06/07/94	1 gallon in form of droplets	1 gallon	Big Sandy River	153 tk received water from a transfer from 73 tk, water turned to steam blew oil (No. 6-oil) out top of tank.
03/09/94	Unknown	Unknown	Chadwick's Creek	Electrical conduit oil was spilled at the RCC.
03/09/94	3 to 4 gallons	1 to 2 gallons	Chadwick's Creek	Oil backed out of electrical conduit manhole onto road during heavy rain. Oil ran to stormwater sewer.
02/06/94	Unknown	20 gallons	Big Sandy River	Oil from the spill that occurred 1/27 was retained in an outfall pipe due to elevated river levels. As the river dropped, approximately 20 gallons reached the discharge point. Most of the oil was retained within a metal boom at the outfall.
01/29/94	10 gallons	10 gallons	Big Sandy River	Oil reached the pond as a result of overfilling the Alky flare knockout drum. As the river raised, it got into the clarifier blowdown pond and hydrocarbons were released into the Big Sandy River.
01/27/94	50 barrels (approx.)	50 barrels (approx.)	Inter-plant lake	A relief valve on an exchanger in the RCC Unit was leaking resulting in hydrocarbon polluting the interplant lake.
01/27/94	50 gallons	50 gallons	Big Sandy River	An overfill of tank 875 at Viney Branch led to the spill, but due to high water the spill did not reach the Big Sandy until 02/06/94.
01/25/94	1 gallon	1 gallon	Big Sandy River	Oil contained in a waste water spill to the upper lake on 01/22/94 traveled to the 006 outfall after the valve separating the upper lake and the Big Sandy was opened to ease flooding.
01/17/94	5 to 10 gallons	5 to 10 gallons	Big Sandy River	Cause and source unknown. Heavy oil was discovered at the 005 outfall contained within the permanent metal boom.

SUMMARY OF FINDINGS

Based on inspection observations, discussions with Ashland personnel, and review of documentation, the following areas of potential noncompliance and areas of concern* with the water pollution control requirements were identified for the time period of January 1994 to October 1996. Additionally, areas of potential noncompliance and areas of concern with the NPDES regulations identified during the laboratory evaluation are presented in the "Laboratory Evaluation" section of this report.

NPDES Permit KY0000388
Part I A. Effluent
Limitations and Monitoring
Requirements

DMRs document 39 daily maximum and 12 monthly average exceedances for Outfall 001, 2 daily maximum exceedances for Outfall 005, 8 daily maximum and 4 monthly average exceedances for Outfall 006, 1 daily maximum exceedance for Outfall 007, 3 daily maximum exceedances for Outfall 008, 1 daily maximum and 1 monthly average exceedance for Outfall 010, 2 daily maximum exceedances for Outfall 011, 2 daily maximum and 1 monthly average exceedance for Outfall 012, 2 daily maximum and 1 monthly average exceedance for Outfall 013, 3 daily maximum exceedances for Outfall 015, 4 daily maximum and 10 monthly average exceedances for Outfall 016, 4 daily maximum exceedances for Outfall 017, 2 daily maximum exceedances for Outfall 018, 3 daily maximum and 2 monthly average exceedances for Outfall 019, 2 daily maximum exceedances for

"Areas of concern" are inspection observations of potential problems or activities that could impact the environment, result in future or current noncompliance with a regulatory requirement or permit, and /or are areas associated with pollution prevention. They may later be determined to be areas of noncompliance as a result of further review and /or consideration of information previously not considered by the inspection team.

NPDES Permit KY0000388
Part I A. Effluent
Limitations and Monitoring
Requirements

Outfall 023, and 4 daily maximum and 2 monthly average exceedances for Outfall 024 during the time period between January 1994 through October 1996.

Ashland failed to conduct the required monitoring for pH, temperature, oil and grease, total organic carbon, chloride, and zinc at Outfall 006 during the month of December 1995. Ashland failed to conduct the required monitoring for TSS and TOC at outfall 023 during June 1994. Ashland failed to conduct the required monitoring for TSS at Outfall 007 for May 1994.

NPDES Permit KY0000388
Part I A. Effluent
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KAR, Title 401, 5:050 (50)

Ashland is not collecting 24-hour composite samples at Outfall 001 in accordance with applicable regulations; samples are time-composited and not proportioned according to flow.

40 CFR § 122.21 (g)(5).

Ashland provided production capacity estimates in their permit application, in lieu of the required (reasonable measure of actual production) information.

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Part II - Standard Provisions
KAR, Title 401, 5:065
Section 1 (13)(d)

Since spring of 1993, Ashland has been bypassing oily wastewater from the MTBE and HF Alky Units around the oil-water separators. No notifications were made to the state.

40 CFR § 110.3

Ashland has discharged oil in harmful quantities to waters of the United States on 15 occasions from January 1994 to June 1996.

40 CFR § 112.4 (a)

Ashland failed to revise its March 17, 1994 SPCC plan within 60 days following two reportable spill events within a 12-month period. Spills were reported on June 7, 1994; June 15, 1994; July 14, 1994; and June 11, 1995.

- No fecal coliform limits are established for the H-Coal sanitary package treatment plant (Internal Outfall 016) when the sanitary effluent is discharged directly to the Big Sandy River via Outfall 015.
- The inability to detect unusual conditions (spills, slug loadings, etc.) at the WWTP quickly enough to divert wastewater to tankage has resulted in treatment upsets and permit violations. Ashland needs to review its internal monitoring program, assess the feasibility of installing in-line monitoring equipment (total organic carbon, pH, etc.), and evaluate the need to provide increased capacity to divert wastewater to storm/surge tanks following the oil-water separators.
- The three oil-water separators do not have functional chain and flight oil and sludge moving devices. Without this equipment, sludge accumulated in the separator cannot be effectively removed without taking the unit out of service, requiring the remaining units to operate at design capacity. The separators cannot be expected to efficiently operate at design capacity for long periods of time with accumulated sludge and inoperable flights. Failure to adequately remove free floating oil could impact the performance of the downstream units, particularly the activated sludge treatment units. Failure to maintain the oil-water separators could be considered a violation of Kentucky Administrative Regulations [KAR, Title 401, 5:065 Section 1 (5) - Proper operation and maintenance], which are incorporated by reference into the NPDES permit.
- The acid feed pumps at the Ashland WWTP have been inoperable for a number of years. Because the refinery has some high pH wastewater sources, including caustic scrubbers, it is possible that high pH

wastewater could be spilled into the refinery sewers. Without acid addition capacity, operators cannot fully adjust pH conditions for optimal biological treatment efficiency.

- Accurate flow data is required for determining compliance with pounds per day permit limits at Outfall 001. During high flow conditions, turbulent conditions occur at the Parshall flume which may introduce greater error into the calculated flows. Additionally, no maintenance records are being maintained on adjustments being made to the bubbler systems for the Parshall flume or rectangular weir.
- Procedures and pH adjustment equipment are inadequate in order to ensure compliance with pH permit conditions for Outfall 006. Until improvements to the pH adjustment equipment are made, it is recommended that the discharge point from the upper lake be equipped with a continuously recording pH meter with alarms, to immediately notify WWTP operators of any discharges outside the permitted pH range.
- Drain valves for secondary containment structures (that discharge to Ashland's sewer system) are left in an open position even during dry weather conditions. If a tank were to overflow or a catastrophic failure were to occur, oil could easily overload Ashland's wastewater treatment facilities. Specific procedures for draining stormwater from these containment structures and maintaining valves in a closed position during dry weather periods need to be developed and implemented.
- Ashland needs to ensure that all secondary containment structures have adequate capacity. Deficiencies were identified by a contractor, and

Ashland could not verify that all corrections have been completed. Additionally, all tank integrity inspections should be completed in accordance with the developed schedule.

- During the inspection, numerous stained soil areas were identified, indicating spills to the environment. Ashland has ceased discharging water draws from the crude tanks to the earthen impoundment, referred to as the crude pond; however, until this area is remediated, it will remain as a source for potential groundwater contamination.
- Ashland's sampling data demonstrate that existing controls and treatment are inadequate to ensure compliance with permitted toxicity limits. Ashland had not assigned staff to coordinate activities and develop specific plans to carry out the required Phase 2 of the Toxicity Reduction Evaluation (TRE) Plan as of the completion of the NEIC inspection. Because Ashland is now in its second mandated TRE, and existing data indicate an inability to eliminate toxicity through operational changes alone, NEIC recommends that treatability studies be initiated concurrently with Phase 2 of the TRE.